

Acknowledgements

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Overview

- What to measure Parameters of concern
- · Identify the problem
- Monitoring Design How to monitor the effectiveness of a BMP
- Sampling Frequency How many samples do I need to collect?
- Sampling Duration How long do I need to collect samples?

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Parameters of Concern

- Nutrients
- Metals
- Sediment
- Pesticides/Herbicides
- Most likely a concern because of the presence of these parameters at concentrations above a water quality standard

Nutrients

- Total nitrogen is the sum of total kjeldahl nitrogen (TKN) plus nitrate (NO₃-) and nitrite (NO₂-)
- TKN is the sum of organic nitrogen and ammonia (NH₃) - in an unfiltered sample represents these forms of nitrogen that are present in solid and dissolved phases, in a filtered sample represents these forms of nitrogen in the dissolved phase
- Organic nitrogen is nitrogen incorporated in organic molecules – proteins (amino acids)

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Nutrients

- Orthophosphate (PO₄³⁻) primary inorganic form of phosphorus in the aqueous phase
- Dissolved phosphorus the sum of phosphorus incorporated in organic molecules and orthophosphate in the aqueous phase
- Total Phosphorus the sum of phosphorus incorporated in organic molecules in solid and aqueous phases and orthophosphate

	Details
Total P	All P forms converted to dissolved ortho-PO and measured.
Ortho-PO ₄	Primary inorganic form of phosphorus
Dissolved organic phosphorus	Dissolved P minus Ortho-P
Total organic phosphorus	Total P minus Dissolved P

Metals

- Total metal in an unfiltered sample, represents the metal present in solid and dissolved phases. EPA drinking water regulations are based on total concentrations.
- Dissolved metal in a filtered sample, represents metal in the aqueous phase only. Biological availability to aquatic organisms is determined by metal in the aqueous phase.

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Sediment-Related Terms

- SSC Suspended Sediment Concentration (mg/L)
- TSS Total Suspended Solids (mg/L)
- TDS Total Dissolved Solids
- Turbidity Nephelometric Turbidity Units
- Gray, J.R., Glysson, G.D., Turcios, L.M., and Schwarz, G.E., 2000: Comparability of suspended-sediment concentration and total suspended solids data, U.S. Geological Survey Water Resources Investigations Report 00-4191, 14p.

SSC, TSS, TDS

- SSC Sediment from natural waters consisting of sand, silt, and clay derived from the weathering and erosion of rocks and soil.
- TSS Derived for wastewater and includes organic material.
- TDS Measure of total amount of dissolved material

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Turbidity

- Measure of water clarity
- Caused by the presence of suspended and dissolved matter
- Includes inorganic particulates (sand, clay, and silt) and organic material such as plankton and organic acids (humic substances)

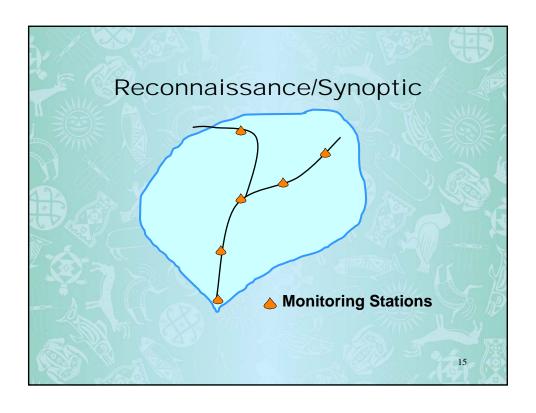
Pesticide/Herbicide

- Targeted compound will often breakdown into other compounds, may need to analyze these compounds as well.
- May need to consider sampling of stream/lake bed sediments and biota to fully understand fate and transport of pesticides/herbicides.

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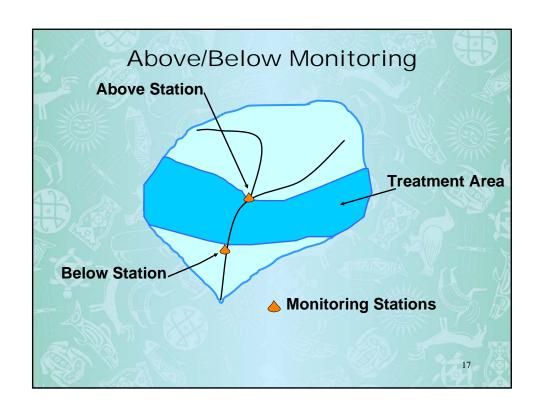
Identify the Problem

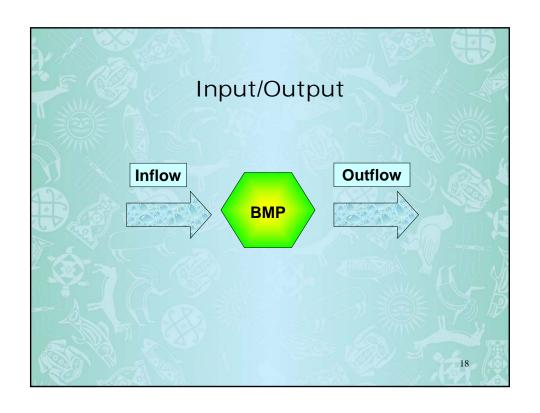
- Reconnaissance/Synoptic Sampling
 - Identify pollutant(s)
 - Identify pollutant source(s)
 - Data collected using EPA 106 funding
 - Data collected from other sources Federal, State, Local Agencies, Universities/Colloges/ Private Consulting Firms



Identify the Problem

- Sampling Locations
 - Mouths of tributaries, on main stem above and below tributaries, and at changes in land use or geology
- Data Analysis
 - Does parameter(s) of concern exceed the appropriate state, federal, or tribal water quality standard for the designated use of the stream or river.
 - Identify sources of high concentrations





Monitoring Design

- Same monitoring design for Above and Below and Input/Output
- Sampling needs to bracket the range of seasonal variability in weather, stream flows, and human activity over the course of a year
- Sample upstream and downstream sites as matched pairs – sample both sites at about the same time and as close in time as possible

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Monitoring Design

- If streamflow is measured can analyze loads as well as concentration
- Mass balance calculation allows for a calculation of pollutant removal efficiency

Hypothesis Test

- Compute differences in concentration between upstream and downstream site (D_i) for each sampling event.
- Null Hypothesis Mean of D_i = 0
- Alternative Hypothesis Mean of Di ≠ 0
- Paired t-test if the differences follow a normal distribution
- Wilcoxon signed-rank test if the differences do not follow a normal distribution
- See Chapter 6 in Helsel, D.R. and Hirsch, R.M., 1992, Statistical Methods in Water Resources, Elsevier, New York, 522 p.

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Sampling Frequency

- Appropriate sample frequency/size varies with the objectives of the monitoring project:
 - Estimation of the mean
 - Detection of change

Mean Estimation

 Determine the sampling frequency necessary to obtain an estimate of the mean for a water quality variable with a certain amount of confidence

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Mean Estimation

$$n = \frac{t^2 s^2}{d^2}$$

where:

- n = the calculated sample size
- t = Student's t at (n-1) degrees of freedom and a specified confidence level
- s = estimate of the population standard deviation
- d = acceptable difference of the estimate from the true mean

Mean Estimation

- t value is taken from a table of Student's t at the desired confidence level (p), typically 0.05 or 0.10).
- Estimate of the population standard deviation is best obtained from baseline data from the monitored water body; if such data are lacking, an estimate from a comparable nearby system can be used.
- Acceptable difference from the true mean is expressed as a percent of the mean.

Calculation may be an iterative process as the value of t may change with the particular value of n chosen

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Mean Estimation - Example

Based on historical monitoring data from Ramirez Brook, how many samples are needed to be within 10 and 20 percent of the true annual mean TP concentration?

- Existing data tell us: Mean = 0.89 mg/L
 Std Dev.= 0.77 mg/L
 n = 165
- The difference (d) for 10% and 20% would be:

 $d = 0.10 \times 0.9 = 0.09 \text{ mg/L}$ $d = 0.20 \times 0.9 = 0.18 \text{ mg/L}$

• The t value for >120 d.f. at p = 0.05 is 1.96

Mean Estimation - Example

For a 10% difference: $n = \frac{(1.96)^2 (0.77)^2}{(0.09)^2} = 281$

Because the t value for n=281 remains 1.96, additional steps are not necessary.

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Mean Estimation - Example

For a 20% difference:

$$n = \frac{(1.96)^2 (0.77)^2}{(0.18)^2} = 71$$

Because the value of t at 70 d.f. is 1.99, a second iteration is necessary:

$$n = \frac{(1.99)^2 (0.77)^2}{(0.18)^2} = 73$$

Mean Estimation - Example

73 samples/yr → mean TP concentration ± 20% of the true mean,

281 samples/yr → mean TP concentration + 10%

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Mean Estimation

Can work backwards to evaluate proposed frequency – knowing n, solve for d:

- For monthly sampling:
- 12 = $(1.78)^2 (0.77)^2$ d = 0.36 \Rightarrow + 40% of true mean (d)²
- For quarterly sampling:
- $4 = (2.13)^2 (0.77)^2$ $d = 0.56 \rightarrow + 62\%$ of true mean $(d)^2$

 If the monitoring objective is to detect and document a change in water quality due to implementation, selected sampling frequency should be able to detect the magnitude of the anticipated change within the natural variability of the system being monitored.

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Minimum Detectable Change

Easy when the groups are very different, when random variability is small, and when the number of samples from each group is large.

Very difficult when the difference or change is very small, when natural variability is large, and when sample numbers are small

$$MDC = t_{(n_{pre} + n_{post} - 2)} \sqrt{\frac{MSE_{pre}}{n_{pre}}} + \frac{MSE_{post}}{n_{post}}$$

Where:

t = the student's t value with $(n_{pre}+n_{post}-2)$ degrees of freedom (in this case selected at p=.05),

n = the number of samples taken in the pre- and post- groups, and

MSE = the mean square error in each period

 $MSE = \sigma^2/n$

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Minimum Detectable Change

Example:

Based on historical monitoring data from the Erod River, annual mean TSS concentration is 36.9 mg/L, with a standard deviation of 2.65 mg/L.

Evaluate the minimum detectable change for weekly, monthly, and quarterly sampling before and after implementation of erosion control measures

Example:

For weekly sampling (n = 52), MSE = 0.135The value of t for 102 d.f. at p = 0.05 is 1.662

= 0.119 = 12%

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Minimum Detectable Change

Example:

For monthly sampling (n = 12), MSE = 0.585The value of t for 22 d.f. at p = 0.05 is 1.717

$$= 0.536 = 54\%$$

Example:

For quarterly sampling (n = 4), MSE = 1.756 The value of t for 6 d.f. at p = 0.05 is 1.943

MDC =
$$1.943$$
 $\frac{1.756}{4}$ + $\frac{1.756}{4}$ = 1.821 = 182%

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Minimum Detectable Change

- •If a reduction of 25% in mean annual TSS concentration is a goal of an implementation project, a weekly sampling schedule could document such a change with statistical confidence, but monthly sampling could not.
- •A reduction of 54% or more in TSS concentration would need to occur to be detected by monthly sampling.
- Quarterly sampling for TSS would be ineffective for this project

MDC analysis can also be applied to designing a posttreatment sampling program if pre-treatment sampling has already been conducted.

However, if the pre-treatment sampling frequency was low, it will be difficult to compensate after the fact.

In the quarterly sampling example, even weekly sampling in the post-treatment period would improve the MDC only to 97%.

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Role of Cost

 Cost should affect but not dictate sampling frequency and duration



- Consider dropping stations and variables to allow adequate frequency and duration
- If cannot afford to do it right...don't do it at all

